



Short communication

Enhanced cycling performance of Al-substituted α -nickel hydroxide by coating with β -nickel hydroxideJinhuan Yao^a, Yanwei Li^{a,b,*}, Yuexiao Li^a, Yanxi Zhu^a, Hongbo Wang^c^a College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, PR China^b Department of Materials Science and Engineering, University of Washington (Seattle), Seattle, WA 98195, USA^c School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210008, PR China

H I G H L I G H T S

- ▶ β -nickel hydroxide-coated Al-substituted α -nickel hydroxide as cathode material for Ni–MH battery is first reported.
- ▶ The coated Al-substituted α -nickel hydroxide combines both the advantages of α -nickel hydroxide and β -nickel hydroxide.
- ▶ The enhancement of the capacity retention of coated Al-substituted α -nickel hydroxide is significant.

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Al-substituted α -nickel hydroxide is modified by coating with pure β -nickel hydroxide in an attempt to improve its cycling performance. The crystal structure and morphology of the prepared samples are examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical performances of the bare and the β -nickel hydroxide coated Al-substituted α -nickel hydroxides are characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and charge/discharge tests. The results show that a β -nickel hydroxide coating on Al-substituted α -nickel hydroxide decreases the charge-transfer resistance and increases the specific discharge capacity. In particular, the enhancement of the capacity retention of β -nickel hydroxide coated Al-substituted α -nickel hydroxide is significant, maintaining 92.5% of the maximum capacity after 100 cycles at a charge/discharge rate of 0.5 C, whereas that of bare Al-substituted α -nickel hydroxide is only 53.6%.

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1. Introduction

Nickel hydroxide compounds are widely used as cathodic active materials in alkaline secondary batteries. Typically, nickel hydroxide has two polymorphic forms, α -Ni(OH)₂ and β -Ni(OH)₂, which transform into β -NiOOH and γ -NiOOH, respectively, in the oxidation process [1]. Currently, β -Ni(OH)₂ is usually used as an active material in alkaline batteries. However, the low theoretical capacity and volume expansion in the β -Ni(OH)₂/ β -NiOOH couple seriously limit the further improvement of the performance of alkaline secondary batteries [2]. In contrast, α -Ni(OH)₂ is capable of realizing a two-electron-exchange reaction in an α -Ni(OH)₂/ γ -

NiOOH couple, which has a much higher theoretical capacity and avoids volume expansion [3]. However, pure α -Ni(OH)₂ is very unstable in strongly alkaline solution and easily transforms into β -Ni(OH)₂, leading to the rapid degradation of the nickel electrode [4]. To stabilize α -Ni(OH)₂, much work has been focused on the partial substitution of Ni ions in the nickel hydroxide lattice by other metal ions, such as Al [5–7], Co [8,9], Fe [10], Mn [11], or Zn [12] ions. Among these metal ions, Al ions are the most attractive because of their high stability in the trivalent state and low cost. The electrolyte used for alkaline secondary batteries is usually concentrated aqueous alkaline solution, and Al ions easily dissolve into the concentrated alkaline electrolyte. Therefore, the Al ion in Al-substituted α -nickel hydroxide may be leached out and enter into the electrolyte [13,14], leading to the transformation of α -nickel hydroxide to β -nickel hydroxide and electrochemical performance degradation [15].

Because β -Ni(OH)₂ has better structural stability and α -Ni(OH)₂ has higher electrochemical activity, α -Ni(OH)₂ coated with β -Ni(OH)₂

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is expected to have better overall electrochemical performance. Based on the above consideration, β -nickel hydroxide was coated on Al-substituted α -nickel hydroxide using chemical precipitation in this work and the electrochemical properties were examined. The results demonstrate that a β -nickel hydroxide coating on Al-substituted α -nickel hydroxide greatly decreases the electron transfer resistance, increases the specific discharge capacity, and significantly enhances the capacity retention of Al-substituted α -nickel hydroxide.

2. Experimental

Al-substituted α -nickel hydroxide was prepared as follows. NaOH solution (1 mol L⁻¹) was added dropwise into a mixture solution containing NiCl₂·6H₂O and Al(NO₃)₃·9H₂O (in a [Ni²⁺/Al³⁺] molar ratio of 5/1) under stirring at 50 °C. After reaction, the precipitate was kept in the mother solution for 19 h at 60 °C and then filtered, rinsed with deionized water, and dried at 60 °C to constant weight. The [Ni²⁺/Al³⁺] molar ratio in the prepared Al-substituted α -nickel hydroxide is 17.2% as determined by energy-dispersive X-ray spectroscopy, which slightly lower than that (20%) in the mother solution. The Al-substituted α -nickel hydroxide was coated with β -nickel hydroxide using a chemical precipitation method using the following procedure. The prepared Al-substituted α -nickel hydroxide powders were dispersed in NiCl₂·6H₂O solution by ultrasonication, forming a suspension. NaOH solution (1 mol L⁻¹) was added dropwise into the above suspension under stirring at 50 °C, producing a β -nickel hydroxide coating on the surface of the Al-substituted α -nickel hydroxide. After reaction, the suspension solution with the coated Al-substituted α -nickel hydroxide was kept for 15 h at 60 °C and then filtered, rinsed with deionized water, and dried at 60 °C to constant weight. The relative mass of β -nickel hydroxide to Al-substituted α -nickel hydroxide was adjusted to 6 wt.%, 10 wt.%, 15 wt.%, and 20 wt.%. The mass of β -nickel hydroxide was calculated from the amount of reactants added under the assumption of 100% conversion efficiency to β -nickel hydroxide. All the reagents were of analytical purity and purchased from Xilong Chemical Factory of Guangdong (Guangdong, China).

The crystal structure of the prepared samples was determined by X-ray diffraction (XRD, Panalytical X'Pert PRO) using a Cu K α radiation source ($\lambda = 1.5418$ Å, 40.0 kV, 100 mA). The surface morphology of the samples was identified by scanning electron microscopy (SEM, Hitachi S-570).

The bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxide powders were mixed with nickel powder, graphite, and acetylene black in a weight ratio of 85/5/5/5 together with a small amount (5 wt.%) of polytetrafluorethylene aqueous solution as binder. Next, the mixture was filled into a nickel foam sheet. The obtained nickel electrodes were dried at 60 °C and then pressed under 8 MPa for 3 min. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using an electrochemical workstation (Autolab PGSTAT12, Eco Chemie) in a three-electrode electrochemical cell employing Hg/HgO as the reference electrode and nickel foam as the counter electrode. The scan rate in the CV measurement was 0.1 mV s⁻¹. EIS measurement was conducted at open-circuit potential (100% depth of discharge) with a superimposed 5 mV sinusoidal voltage in the frequency range from 10 kHz to 10 mHz.

Charge/discharge studies were conducted in simulated batteries, including the prepared nickel hydroxide electrode as the cathode, a hydrogen-storage alloy electrode as the anode, and polypropylene as the separator between the cathode and anode. The electrolyte solution consisted of 6 mol L⁻¹ KOH. The battery

was cathodically limited. The galvanostatic charge/discharge characteristics of the simulated batteries were recorded with a Land battery performance testing instrument (CT2001C) at ambient temperature. The batteries were charged at a rate of 0.5 C (180 mA h g⁻¹) for 2.4 h and discharged at the same rate down to a cut-off voltage of 1.0 V.

3. Results and discussion

Fig. 1 shows the XRD patterns of the bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxides. When the amount of coating is less than 10 wt.%, all of the diffraction peaks can be indexed as α -Ni(OH)₂ (ICDD–JCPDS 38–715). Characteristic peaks for β -nickel hydroxide are not distinctively observed because the proportion of β -nickel hydroxide is much smaller than that of Al-substituted α -nickel hydroxides. When the coating exceeds 15 wt.%, the diffraction peaks from β -nickel hydroxide are observed.

Fig. 2 displays the SEM photographs of the bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxides. All samples consist of dense particles with irregular shapes, which is very similar to the Al-substituted α -nickel hydroxide powders prepared by homogenous precipitation [16] and electrochemical impregnation [17]. The formation of such irregularly shaped Al-substituted α -nickel hydroxide is a subject for further study; however, a possible mechanism might be as follows. During the precipitation process, the deposition of Al cations in the Ni(OH)₂ lattice proceed more quickly than that of Ni cations because the Ksp of Al(OH)₃ (1.3×10^{-33}) is much smaller than that of Ni(OH)₂ (5.5×10^{-16}). This difference results in the heterogeneous agglomeration of crystallite from all directions and the formation of irregular shapes. With increasing coating amounts, the surface of Al-substituted α -nickel hydroxide seems to be coarse. However, it is still difficult to distinguish the α -nickel hydroxide and β -nickel hydroxide directly from the SEM images.

Fig. 3a shows the cyclic voltammograms of bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxide electrodes at a scan rate of 0.1 mV s⁻¹. As the amount of β -nickel hydroxide coating increases from 0 to 10 wt.%, the oxidation peak potentials of nickel hydroxide electrodes shift from 0.57 V to 0.59 V and the reduction peak potentials remain at 0.29 V. Further increasing the amount of β -nickel hydroxide coating from 15 wt.% to 20 wt.%

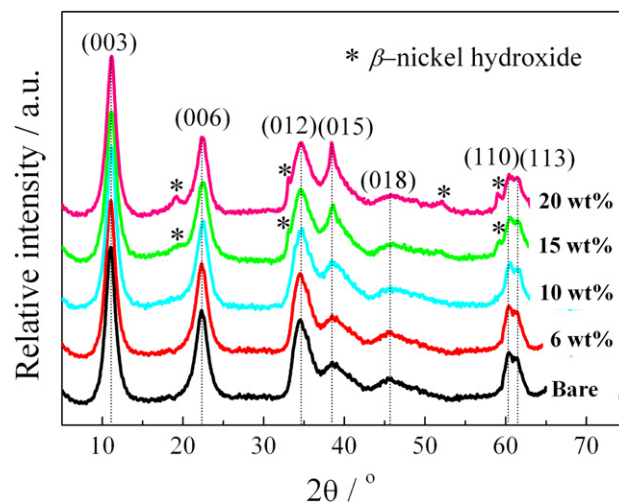


Fig. 1. XRD patterns of bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxides.

induces a negative significant shift of both the oxidation peak and reduction peak potentials of the nickel hydroxide electrodes relative to the bare Al-substituted α -nickel hydroxide electrode. For example, the oxidation peak potential (0.52 V) and reduction peak potential (0.27 V) of the 20 wt.% β -nickel hydroxide coated Al-substituted α -nickel hydroxide electrode are 50 mV and 20 mV more negative than the corresponding oxidation peak potential (0.57 V) and reduction peak potential (0.29 V) of the bare Al-substituted α -nickel hydroxide electrode. Generally, both the oxidation peak potential and the reduction peak potential are more negative than the corresponding peak potentials of Al-substituted α -nickel hydroxide electrode [18]. Therefore, the 15 wt.% and 20 wt.% β -nickel hydroxide coated Al-substituted α -nickel hydroxides tend to present the characteristics of β -nickel hydroxide. In comparison, both the oxidation and reduction peak areas of the β -nickel hydroxide coated Al-substituted α -nickel hydroxide electrodes are larger than those of the bare one, indicating that surface modification improves the electrochemical activity of Al-substituted α -nickel hydroxide, which is further supported by the following charge/discharge results. Fig. 3b presents the Nyquist plots of the bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxide electrodes at the stable open-circuit potential of 100% depth of discharge. The calculated charge-transfer resistances (R_{ct}) of the bare, 6 wt.%, 10 wt.%, 15 wt.%, and 20 wt.% β -nickel hydroxide coated Al-substituted α -nickel hydroxides are 1.63, 1.03, 0.54, 0.85, and 0.98 Ω , respectively. This finding implies that the electrochemical reaction within the β -nickel hydroxide coated Al-substituted α -nickel hydroxide occurs more easily than that within the bare electrode. Because β -nickel hydroxide has a much smaller interlayer spacing (approximately 4.60 Å), the β -nickel hydroxide coating is believed to block the de-intercalation of interlayer anions and water molecules from Al-substituted α -nickel hydroxide. These reserved interlayer anions and water molecules

provide a relay system for the proton diffusion in the electrode [19]. Thus, the solid-state proton diffusion and intercalation/de-intercalation processes are remarkably improved, leading to a higher electrochemical activity and lower charge-transfer resistance.

Fig. 4a presents the 40th charge/discharge curves of the bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxide electrodes at 0.5 C. The β -nickel hydroxide coated Al-substituted α -nickel hydroxide electrodes show higher specific discharge capacities than the bare electrode. In particular, the Al-substituted α -nickel hydroxides coated with 10 wt.% β -nickel hydroxide presents the highest specific discharge capacity of 317.6 mAh g⁻¹, which is 70.0 mA h g⁻¹ higher than that (247.6 mAh g⁻¹) of the bare electrode. In addition, the discharge plateau of the Al-substituted α -nickel hydroxide coated with 10 wt.% β -nickel hydroxide is higher than that of all other electrodes. Fig. 4b shows the cycling performance of the bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxide electrodes at 0.5 C. The initial specific discharge capacities of the bare, 6 wt.%, 10 wt.%, 15 wt.%, and 20 wt.% β -nickel hydroxide coated Al-substituted α -nickel hydroxides are 292.6, 308.1, 331.0, 320.3, and 285.5 mA h g⁻¹, respectively. After 100 cycles, the capacity retentions of the bare, 6 wt.%, 10 wt.%, 15 wt.%, and 20 wt.% β -nickel hydroxide coated Al-substituted α -nickel hydroxides are 53.6%, 88.4%, 92.5%, 91.6%, and 81.5%, respectively. Thus, the cycling performance of Al-substituted α -nickel hydroxides is greatly enhanced by surface modification with β -nickel hydroxide.

The higher discharge capacity and better cycling performance of β -nickel hydroxide coated Al-substituted α -nickel hydroxide are due to its unique structure. Because β -nickel hydroxide is very stable in strongly alkaline electrolyte, the β -nickel hydroxide coating is believed to prevent the dissolution of Al ions by

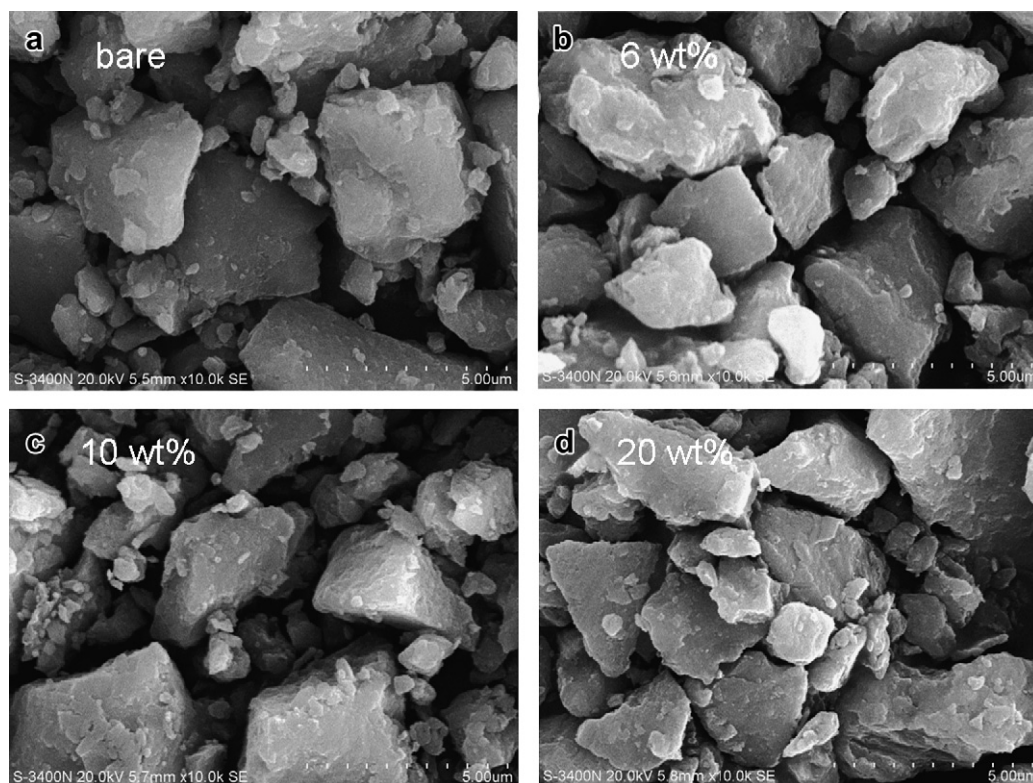


Fig. 2. SEM images of (a) bare, (b) 6 wt.%, (c) 10 wt.%, and (d) 20 wt.% β -nickel hydroxide coated Al-substituted α -nickel hydroxides.

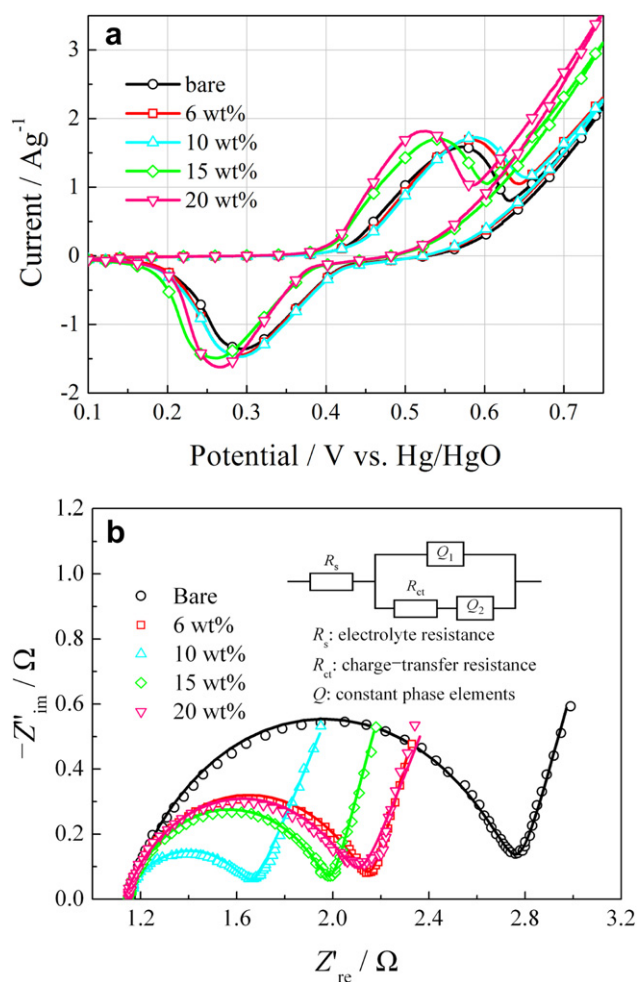


Fig. 3. (a) Cyclic voltammograms and (b) Nyquist plots of bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxides. In Nyquist plots, the symbols and solid lines correspond to the experimental data and fitting curves, respectively.

reducing the direct contact between Al-substituted α -nickel hydroxide and the electrolyte. Therefore, the cycling performance of β -nickel hydroxide coated Al-substituted α -nickel hydroxide is enhanced significantly. It is worth noting that increasing amounts of β -nickel hydroxide coating on Al-substituted α -nickel hydroxide tend to decrease the discharge capacity because β -nickel hydroxide is less active than α -nickel hydroxide. Thus, when the amount of coating increases from 15 wt.% to 20 wt.%, the charge-transfer resistance increases and the discharge capacity decreases.

To the best of our knowledge, this study is the first instance of improving the electrochemical performance of Al-substituted α -nickel hydroxide by coating it with β -nickel hydroxide. This method has the following advantages: (1) the coating material (β -nickel hydroxide) is also electrochemically active, unlike the electrochemically inert materials explored in most of the previous investigations [20–24]; (2) the β -nickel hydroxide coating, which has very good stability in strongly alkaline electrolyte, can prevent direct contact between Al-substituted α -nickel hydroxide and the electrolyte and therefore enhance the phase structure stability of α -nickel hydroxide; (3) the synthesized material combines the advantages of β -nickel hydroxide and α -nickel hydroxide; and (4) the facile synthesis procedure is favorable for large-scale production.

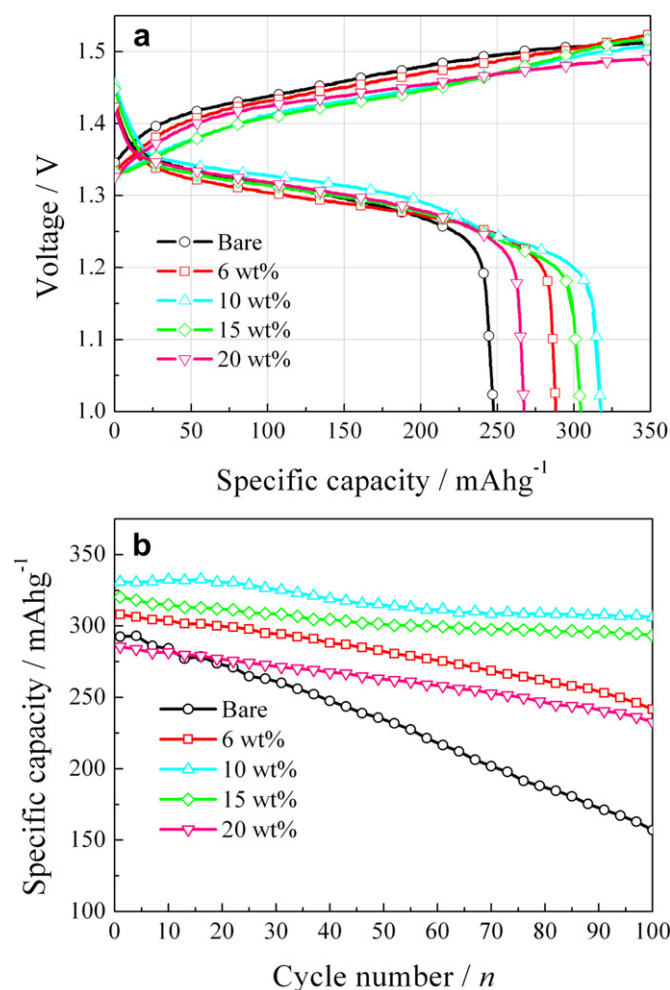


Fig. 4. (a) Charge/discharge curves and (b) cycling performance of bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxides at 0.5 C.

4. Conclusions

Al-substituted α -nickel hydroxide was coated with β -nickel hydroxide by chemical precipitation. The electrochemical performances of bare and β -nickel hydroxide coated Al-substituted α -nickel hydroxides were investigated and compared. The results demonstrate that a β -nickel hydroxide coating on Al-substituted α -nickel hydroxide decreases the electron transfer resistance, increases the specific discharge capacity, and significantly enhances the capacity retention of Al-substituted α -nickel hydroxide. In particular, the 10 wt.% β -nickel hydroxide coated Al-substituted α -nickel hydroxide shows the best electrochemical performance. The superior performance of β -nickel hydroxide coated Al-substituted α -nickel hydroxide is attributed to the reduced contact between the Al-substituted α -nickel hydroxide and the electrolyte, mitigating the degradation of Al-substituted α -nickel hydroxide.

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